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ScienceDirect
Energy Procedia 4 (2011) 3239–3245
Energy Procedia
www.elsevier.com/locate/procedia

GHGT-10

The challenge of predicting groundwater quality impacts in a CO_2 leakage scenario: Results from field, laboratory, and modeling studies at a natural analog site in New Mexico, U.S.A.

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Abstract

A vital aspect to public and regulatory acceptance of carbon sequestration is assurance that groundwater resources will be protected. Theoretical and laboratory studies can, to some extent, be used to predict the consequences of leakage. However, direct observations of CO_2 flowing through shallow drinking water aquifers are invaluable for informing credible risk assessments. To this end, we have sampled shallow wells in a natural analog site in New Mexico, USA, where CO_2 from natural sources is upwelling from depth. We collected major ion, trace element, and isotopic (^3H, ^{18}O, and Sr) data and, coupled with laboratory experiments and reactive transport modeling, have concluded that the major control on groundwater quality at this site is not chemical reaction of CO_2 with the aquifer but intrusion of saline waters upwelling with the CO_2.

Using reactive transport modeling based on field data, we show the difference in reactivity of the CO_2 and CO_2/saline water source terms, particularly with respect to carbonate mineralogy. Sr isotopes were used to investigate whether aquifer waters were affected by carbonate mineral reaction with CO_2 or by saline water intrusion. Preliminary data suggest that Sr isotopes can successfully be used to discriminate between the two types of source terms at Chimayó; this technique shows promise for monitoring CCS sites.

In developing predictive capabilities for future sites, it is critical to identify the solid phases and specific reactions controlling dissolved trace metal concentrations in both the presence and absence of CO_2. We have conducted laboratory experiments to identify these phases and have found that some elements (e.g., U, Ca) are largely controlled by ion exchange and/or carbonate minerals. In the experiments, the concentration of some metals increases after exposure to CO_2 (although concentrations remain below the U.S. EPA primary drinking water standards); we are currently extending these experiments to determine if the reactions causing the increase are reversible and, if so, on what time scales. Metal scavenging by secondary mineral precipitation, as observed at other natural analog sites, may be important at certain temporal scales.

We are using the information gained from this field and laboratory study to develop predictive models for application to risk assessment at future CCS sites. The models will be particularly useful in identifying the temporal and spatial scales of water quality changes and in developing possible mitigation strategies in the case of leaks at engineered CCS sites.

doi:10.1016/j.egypro.2011.02.242

1. Introduction

Groundwater protection is of vital importance to CCS projects. While risk assessment requires quantitative information about the potential impact of CO_2 leakage on overlying aquifers, the consequence of such leakage is largely unknown. In this study, we examine a natural analog site where CO_2 flows through a shallow drinking water aquifer in order to assess the impact of CO_2 leakage on groundwater quality and to build numerical models that will predict such impacts at CCS sites. We use field and laboratory studies to assess the mechanisms that control changes in groundwater chemistry and incorporate these mechanisms into a reactive-transport simulation model. We use the simulation model to illustrate a range of scenarios that might occur at a CCS site, and to identify the types of data that would be most useful to collect in a site characterization effort to support development of effective predictive models.

One possible impact of CO_2 on groundwater quality is pH depression and trace metal mobilization, as was observed during controlled CO_2 release experiment in a shallow aquifer [1]. Modeling studies by Wang and Jaffe [2] clearly show the potential for this effect and also demonstrate the large uncertainties associated with model predictions, primarily due to uncertain reaction kinetics. It is still largely unknown, however, how a 'trace metal plume' induced by CO_2 leakage would evolve in time and space. Making even naïve predictions of these details will be necessary for risk assessment and monitoring network design.

Previous analysis and modeling of groundwater samples collected at the natural analog site suggest that the dominant mechanism producing poor groundwater quality is brine co-transported with CO_2; this brine not only causes high TDS but also elevated trace elements (U, As, F) concentrations [3]. For the purposes of this paper we focus on a single trace element: uranium. Uranium is locally abundant in the New Mexico aquifer used in our natural analog study and hence could potentially be mobilized (or immobilized) by geochemical changes induced by CO_2 flow. Although uranium *per se* may not be a common trace element of concern at many CCS sites, we expect the issues raised by our study of U to be widely applicable to other sites where trace element mobilization is a concern.

2. Natural analog site

The natural analog site is a shallow aquifer near Chimayó, New Mexico, USA. The aquifer lies within a sub-basin of the Rio Grande Rift. The rift is a zone of anomalous heat flux with local emergence of thermal water and CO_2 gas. In one location near Chimayó, a shallow well geysers 99.9% pure CO_2 daily [4]. Many of the drinking water wells in the vicinity have high levels of dissolved CO_2 and thus this site is ideal for studying the effects of CO_2 flux on groundwater quality.

The aquifer consists of Miocene-age alluvial fan deposits known as the Santa Fe Group. The Santa Fe Group sediments include layers of sands, gravels, and clays, dissected by numerous north/south trending faults. The aquifer is predominately unconfined, yet contains locally compartmentalized zones which are overpressured. With few exceptions, the groundwater is oxidizing. Faults, which often contain silicate or carbonate cement, can behave as barriers to flow. Some faults, however, may serve as conduits for upward migration of CO_2. The aquifer is underlain by a Paleozoic-age carbonate layer. Numerous lines of evidence suggest this layer is discontinuous. The mineralogy of the Santa Fe group sandstone is dominated by quartz and feldspars with ubiquitous secondary calcite cement.

3. Field studies

Groundwater in the Chimayó area was first sampled by Cumming [4], who measured field parameters (dissolved oxygen, pH, temperature, conductivity) and analyzed samples in the laboratory for major elements, ^{2}H, and ^{18}O. Gas samples from the geyser well were also analyzed for major and trace elements. In an earlier study, we resampled many of these wells and several new wells in 2004-2007 and analyzed for major and trace elements, as well as ^{2}H, ^{18}O, and ^{13}C [3]. For this study, a third round of groundwater sampling occurred in 2009 for eight wells

[5]. Prior to sampling, each well was pumped thoroughly or allowed to run until temperature and TDS remained consistent. Samples for isotopic analysis were filtered into acid-cleaned bottles and preserved with ultrapure nitric acid. Strontium isotope work was carried out at the University of Pittsburgh. Sr was purified and concentrated under clean lab conditions following the procedure described in Hamel et al.[6]. Sr isotopic composition was determined on a Finnigan MAT 262 multicollector thermal ionization mass spectrometer. External reproducibility is equal to or better than ±20 ppm (2 sigma). The $^{87}Sr/^{86}Sr$ ratio for SRM987 for the period of the analyses was 0.71024.

Results from the most recent sampling round indicate that Sr isotopes can be sensitive indicators of subsurface processes related to CO_2-water-rock interaction. Despite their spatial proximity, well waters in the Chimayó area exhibit large variations in $^{87}Sr/^{86}Sr$ (0.70980-0.71764). Well waters with <0.25 g/L CO_2 fall on a Sr isotope mixing curve that indicate admixture of 1 to 10% high-CO_2 brine. Two neighboring wells northwest of the main fault, one with anomalously high dissolved CO_2 and high TDS, have similar $^{87}Sr/^{86}Sr$ ratios that are significantly lower than the CO_2-brine value. This suggests that a CO_2-resistant barrier divides a lithologically and isotopically distinct aquifer unit tapped by these wells; leakage of CO_2 into one side could result in increased dissolution of aquifer carbonate cement [5].

4. Laboratory studies

Two sets of experiments were performed using aquifer samples collected at outcrops in several locations in the Chimayó area. Special effort was made to sample the lithologies most likely be present in the water bearing zones (lithosomes A and B [3]). In the first set, samples were placed either in pure water or a synthetic water approximating the same major ion composition as typical Chimayó groundwater, then CO_2 gas was bubbled into the sample. Over time, pH was measured, and water samples were collected and analyzed for major and trace elements. These data were reported in Carey et al.[7]; a few key time series are reproduced here in Figure 1. After an initial equilibration period, CO_2 was added and pH abruptly dropped from 7.8 to 5.8. Immediately, both [Ca] and [U] increased. Eventually, pH began to rise and both [Ca] and [U] decreased to approximately pre-CO_2 levels. At this point in time, HCl was added to the solution; the data collected after this point in time are the focus of ongoing study and are not addressed here. The trends in pH and Ca (pre-HCl) could be caused by the addition of CO_2 and some degree of buffering by carbonate dissolution and precipitation. The measured trends in U could either be caused by pH-driven sorption/desorption reactions or by precipitation/dissolution with a solid-solution U-carbonate mineral [8]. We explore both possibilities in reactive-transport modeling described below.

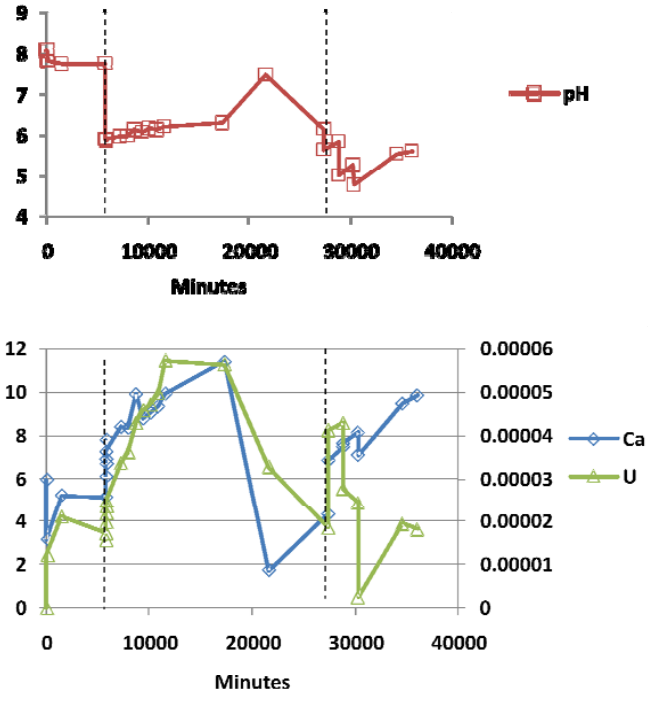

Figure 1. Experimental results

The second set of experiments performed was a series of sequential extractions conducted on the sediment samples. The goal of these extractions was to provide insight into the particular form of the trace elements in the sediments and to infer probable mechanisms by which trace metals could be released into solution. Outcrop solids were crushed and sieved to < 100 mesh. Sequential extraction leaching protocols were developed based on prior literature [9,10]. Sample extracts were analyzed for major elements using inductively coupled plasma (ICP) optical emission spectroscopy (OES) and ICP-mass spectrometry (MS). In one set of extractions, samples from both Lithosome A and Lithosome B were reacted sequentially to determine the water-soluble (ultrapure water, Milli-Q, 18.2 MΩ/s), exchangeable (1.0 M ammonium acetate, pH 7), and carbonate (0.11 M acetic acid) fractions (Figure 2).

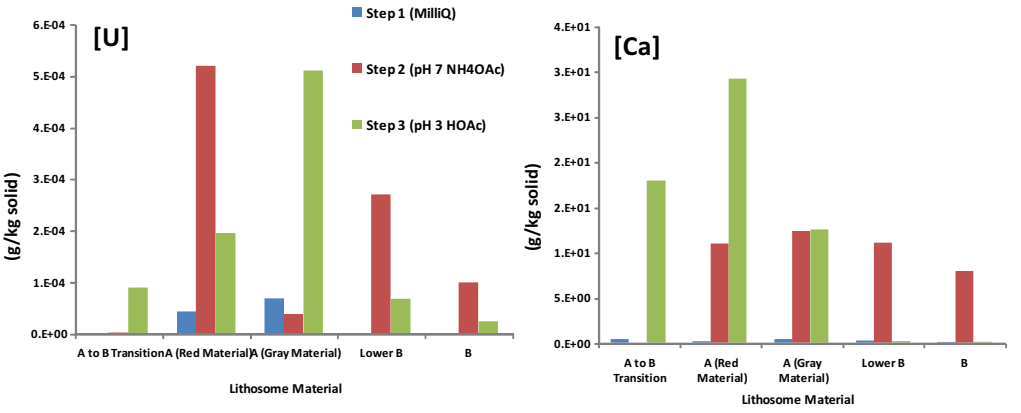

Figure 2. Extraction results

These results show that U may either be desorbed from mineral surfaces (e.g., “exchangeable” fraction) or released through dissolution of carbonate minerals.

In another set of extractions, samples from both lithosomes were reacted sequentially to determine the exchangeable/carbonate (0.11 M acetic acid), reducible minerals, e.g. manganese and iron oxides, (0.5 M hydroxylamine HCl), and oxidizable components, e.g. pyrite (hydrogen peroxide under heat followed by 1.0 M ammonium acetate leach) fractions (Figure 3). These data also show that U is mainly present in exchangeable/carbonate fractions (except for the gray material found in Lithosome A, where U predominantly is

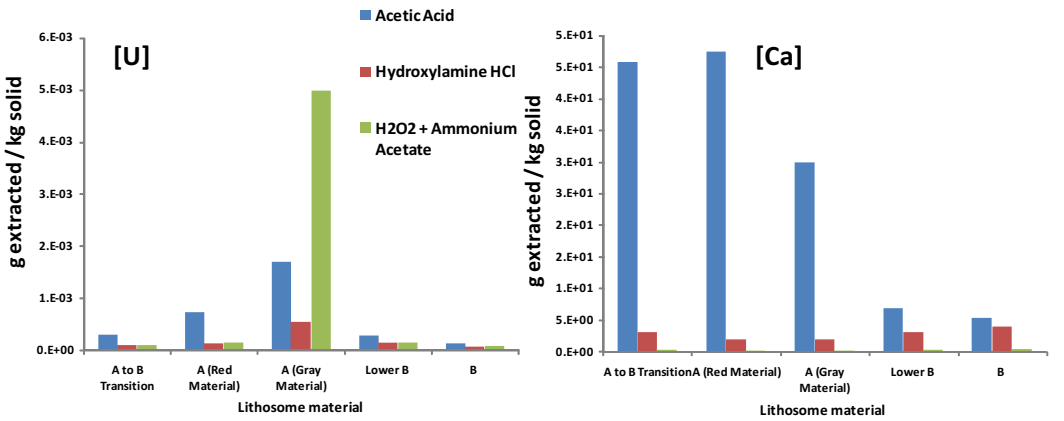

Figure 3. Extraction results

found in the oxidizable fraction). Results from these sequential extractions suggest that carbonate minerals present in the Chimayó aquifer may serve as sources of U input into Chimayo groundwater during reaction of aquifer minerals with intruding CO_2. Also, significant geochemical heterogeneity is evident; this could be an important factor to consider in developing numerical models of CCS sites.

5. Reactive transport modeling.

The studies described above were used to construct 1-D reactive transport models, using the finite-volume code FEHM [11]. The models were designed to reproduce the key features of the Chimayó aquifer: deep brine and CO_2 upwelling along a fault into a shallow sandstone aquifer, in accordance with the conceptual model of groundwater flow presented in Cumming [4] and Keating et al. [3] (Figure 2). We assign initial water chemistry to the two layers in accordance with measured field data from the sandstone aquifer and inferred carbonate/brine water from geochemical models constrained by field data [3] Table 1). Because the experimental data suggests that some or all the U is released from carbonate minerals, we simulated a solid-solution U-carbonate mineral with a molar ratio of U:Ca equal to that measured in our extraction experiments: ~2.E-7. This is a reasonable estimate of carbonate composition in the sandstone cements, but may underestimate the amount present in carbonates in the deeper layers. We assume the solid-solution carbonate mineral has the same K_{eq} as pure calcite. We include the aqueous uranium complexes considered by Dong et al. [12] and Hsi and Langmuir [13] and sorption reactions generalized from Hsi and Langmuir [13]. We found that under all circumstances, aqueous U was dominated by the $Ca_2UO_2(CO_3)_3$ complex, which were shown by Dong et al. [12] to suppress U sorption. For this reason, our simulations suggested that sorption does not occur under these geochemical conditions. To simplify the calculations, we subsequently removed sorption reactions from the simulations.

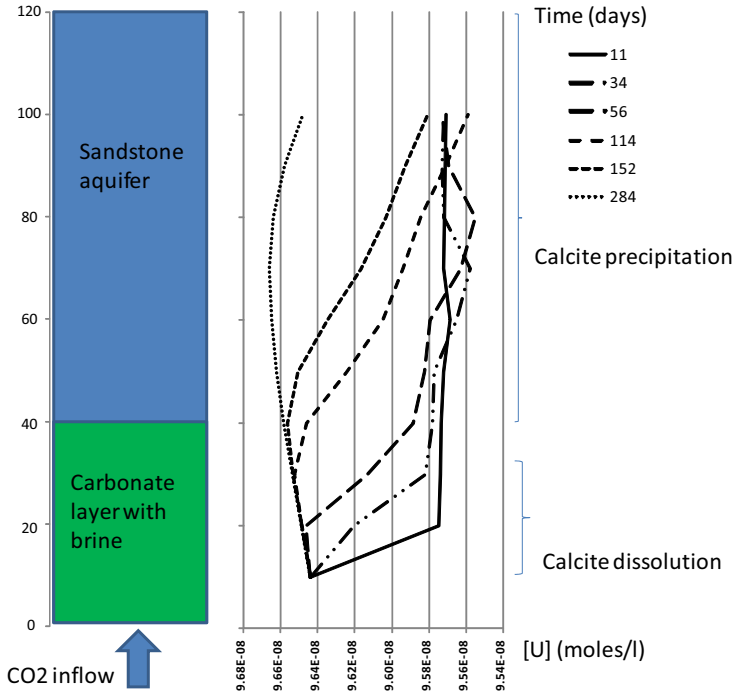

Figure 4. Reactive transport model results for relatively low U:Ca ratio in all layers

W 'so neglected redox reactions, field data suggests that most ; are oxiding. CO_2 was only considered in the dissolved phase.

In Figure 4, we show the predicted evolution of [U] in the column. Interestingly, U concentrations in the upper nodes, corresponding to the shallow sandstone aquifer, initially decline. This is due to carbonate mineral *precipitation*, as a result of upward advection of the higher pH/high alkalinity water below and disequilibrium with the local water. This precipitation, in fact, continues throughout the simulation. However, after about 100 days the [U] increases above the initial conditions, due to advection of higher [U] concentration water originating below. The dominance of advective transport of [U], in contrast to *in situ* reaction–driven changes, suggested by this simulation result, is consistent with interpretation of field data trends presented in Keating et al. [3].

To investigate the sensitivity of this result to assumptions about the U content of the deeper carbonate layer, we increased the molar ratio U:Ca to 10^{-6} in the deep layer. The results are shown in Figure 5. There are several interesting differences between this and the previous figure. First, the peak concentrations are much larger than the previous results. This is a direct consequence of the higher assumed U content of the deeper rock. Second, the highest concentrations only persist during intermediate times. At later times, this pulse has left the system and concentrations return to pre-leak levels. The length of time the high concentrations persist is related to many variables, including the molar ratio assumed for the deep layer.

6. Discussion and Conclusions

Previous analysis and modeling of groundwater samples collected at a natural analog site suggest that the dominant mechanism producing poor groundwater quality is brine co-transported with CO_2; this brine not only causes high TDS but also elevated trace elements (U, As, F) concentrations [4]. However, exposing Chimayó sediments to CO_2 in the laboratory under controlled conditions clearly show that pH is depressed and trace elements are released [7]. We hypothesize that the differences between these results lies not only in geochemical differences between laboratory conditions and the more complex field setting but also the very different time scales the two data sets represent. We have developed reactive-transport models to assist in explaining these observations and to build towards developing a framework for generic predictive models useful for risk assessment at CCS sites. For the purposes of this study, we focus on uranium.

A sequence of extraction experiments indicates that the probable source of U in the sandstone aquifer is carbonates. This is consistent with the laboratory experiments that show that as pH drops, both [Ca] and [U] increase. Reactive-transport modeling, using site-specific water chemistry and aquifer mineralogy data, suggests that sorption is generally suppressed by complexation with [Ca] and so sorption is unlikely to be an important mechanism. Complex sorption effects such as competition with Fe-oxides are not considered here, but cannot be eliminated as potentially influential processes. For the purposes of this study, however, we focused on a single hypothesis:that precipitation/dissolution of Ca-U solid solutions in carbonates as controlling [U] concentrations in the shallow aquifer through modeling.

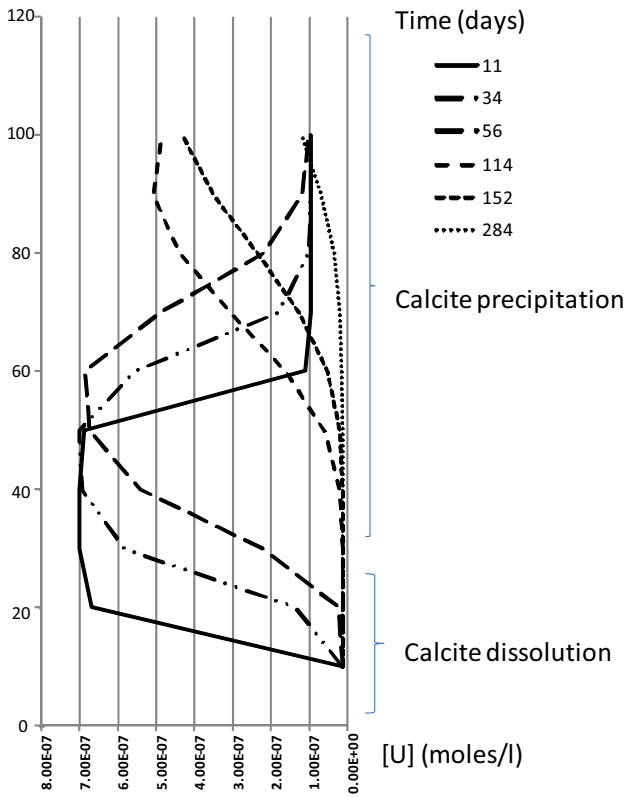

Figure 5. Simulation results for higher U:Ca molar ratio presumed for lower carbonate rocks

One-dimensional models of a two-layer system exposed to a CO_2 source from below the shallow aquifer show that [U] initially declines as the CO_2 influx progresses upward. This is due to disequilibrium between the shallow aquifer and lower carbonate aquifer waters, which are carried upward with the CO_2. Eventually, [U] rises, but not because of *in situ* reactions (calcite dissolution), but because of U advection with the rising water. This result is consistent with conclusions of Keating et al. [3], which emphasized the role of the deeper water in controlling trace element concentrations.

A sensitivity analysis showed the importance of the assumed composition of the solid-solution calcite. If the deeper rocks are assumed to have a higher U:Ca molar ratio, shallow [U] can increase to relatively large levels. However, simulations suggest that this would be a transient effect.

These results highlight the importance of considering spatial and temporal trends in groundwater chemistry changes associated with a CO_2 leak. Monitoring strategies should be developed in this context. Our results also highlight the importance of basic characterization of not only the shallow aquifers but also the deeper layers below. This is because geochemical interactions within deeper layers as the CO_2 migrates upward may have a greater influence on shallow aquifer quality than *in situ* reactions within the aquifer. This result could be generalized to stratigraphic settings where shallow dilute aquifers are underlain by older sediments containing relatively high TDS waters and rocks with significant trace element concentrations. This type of stratigraphic setting is very common in the U.S.A.

7. Acknowledgements. This work was funded by the U.S. DOE ZERT (Zero Emission Research and Technology) program. We appreciate helpful discussions with Dennis Newell.

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